

UNCLASSIFIED

AD NUMBER

AD841951

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors;  
Administrative/Operational Use; SEP 1968. Other requests shall be referred to Office of Naval Research, Arlington, VA 20360.

AUTHORITY

ONR ltr 27 Jul 1971

THIS PAGE IS UNCLASSIFIED

AD841951

**MONSANTO/WASHINGTON UNIVERSITY**

**ONR/ARPA ASSOCIATION**

**THE EFFECT OF TEMPERATURE ON THE DELAYED  
YIELD AND FAILURE OF "PLASTICIZED" EPOXY RESIN**

O. Ishai

September 1968

**PROGRAM MANAGER**

**ROLF BUCHDAHL**

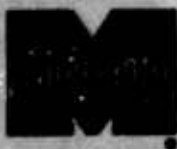
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Director of Material Sciences, Office of Naval Research. *Wash D.C. 20360*

**MONSANTO RESEARCH CORPORATION**

A SUBSIDIARY OF MONSANTO COMPANY

800 N. LINDBERGH BOULEVARD

ST. LOUIS, MISSOURI 63166



ADDRESSION for	
WPSY	WHITE SECTION <input type="checkbox"/>
WDC	DIFF SECTION <input checked="" type="checkbox"/>
WHA'NOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
BY SECTION/AVAILABILITY CODES	
DIST.	AVAIL. and/or SPECIAL
g	

## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

DDC release to CFSTI is not authorized.

HPC 68-59

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION

Sponsored by ONR and ARPA

Development of High Performance Composites

THE EFFECT OF TEMPERATURE ON THE DELAYED  
YIELD AND FAILURE OF "PLASTICIZED" EPOXY RESIN

O. Ishai

September 1968

Rolf Buchdahl, Program Manager

Monsanto Research Corporation  
800 North Lindbergh Boulevard  
St. Louis, Missouri 63166

This document was prepared under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 873, ONR Contract Authority NR 356-484/4-13-66, "Development of High Performance Composites."

## FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 873, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (phone 314-694-4721).

The contract is funded for \$5,000,000 and expires 30 April 1970.

# THE EFFECT OF TEMPERATURE ON THE DELAYED YIELD AND FAILURE OF "PLASTICIZED" EPOXY RESIN\*

O. Ishai\*\*  
Washington University  
St. Louis, Missouri

## Abstract

Epoxy-versamid specimens were loaded in tension up to failure at different constant strain-rates and temperatures. Results revealed three modes of behavior prevailing at different temperature-strain-rate regions and associated with brittle, ductile and rubbery failure modes. The ductile region was found to be confined within a narrow band on the temperature-strain-rate plane, and is characterized by a yield plateau in the stress-strain curve and by linear dependence of yield stress on log strain rate and temperature. Yield strain seems to be almost unaffected by strain-rate, but decreases slightly with temperature rise.

Analysis indicated that experimental data within the ductile region are consistent with Eyring's formulation for non-Newtonian viscoplastic flow. It leads to the evaluation of the "apparent activation energy" and activation volume for the two epoxy systems tested.

Comparison with previous work indicates that the above parameters as well as yield stress and elastic modulus tend to increase with the decrease of the versamid content in the resin.

---

\*Sponsored by the Advanced Research Projects Agency, Department of Defense under Office of Naval Research.

\*\*On sabbatical leave, Technion, Israel Institute of Technology

# THE EFFECT OF TEMPERATURE ON THE DELAYED YIELD AND FAILURE OF "PLASTICIZED" EPOXY RESIN

O. Ishai

## Introduction

Yield and failure mechanisms of solid polymers have attracted much attention during recent years. Such a study was found to be a useful means for understanding molecular structure and processes as well as for specification of these materials for engineering structural design. From both physical and engineering viewpoints, temperature and time are considered the main factors affecting the mechanical properties and especially the strength limits of polymeric systems. The macroscopic yielding of solid polymers, which was found to prevail at the glassy and transition zone, can be viewed as viscoplastic flow at a constant strain-rate under constant stress level. Such a non-Newtonian flow is activated at high mechanical energy level by the principal shear stress component [1-3], according to the Eyring's formulation [4]. Such yield characteristics have been found for linear amorphous [5-7] and semi-crystalline [8-10] as well as for cross-linked [11] glassy polymers.

Several studies deal with the effect of temperature and time on the tensile strength of elastomers under creep [12], constant strain rate [13], and relaxation [14] test modes. The results indicate that failure-time characteristics can be analyzed by means of time-temperature superposition principle. It was suggested recently [15] that yield data could also be treated by a similar time-temperature shift analysis. Eyring's rate-process hypothesis, on the other hand, though being limited to a certain

time-temperature range, is believed to be a useful means for macro-rheological analysis as well as for physical micro-interpretation of the yielding process.

Yield characteristics of an epoxy-versamid system at room temperature was found to be consistent with the above approach under both constant strain rate (C.S.R.) and creep test modes in tension, compression, and flexure [16]. The strong viscoplastic nature of this resin was attributed to the versamid component, which is believed to serve as an internal plasticizer in this cross-linked copolymer [17]. Epoxy-versamid resin was found to provide a matrix of good adherence and high toughness in epoxy-glass composites at room temperature [18]. The main objective of the present work is the study of the temperature effect on the yielding process and on the extent of the ductile behavior of this resin. Another purpose is to learn more about its mechanical performance at higher temperatures.

#### Experimental Details

Specimens were made of two epoxy mixes consisting of: Shell epon<sup>®</sup> 815 and versamid<sup>®</sup> 140 with the weight proportions of 60/40 and 70/30, respectively. Mixing was conducted under vacuum, followed by a casting between two glass plates and cured for 30 minutes at 100° C followed by 3-1/2 hours at 150° C. Tensile specimens were cut from the 1/8" plates according to A.S.T.M. D 638-64T.

#### Test Procedure

Specimens were loaded in tension by the Instron tester equipped with a temperature-controlled chamber. Constant strain rate (C.S.R.) ranged from about



$5 \times 10^{-4}$  up to  $0.5 \text{ min}^{-1}$ . Constant temperature levels ranged from  $5^\circ \text{ C}$  up to  $75^\circ \text{ C}$  having the accuracy of  $\pm 0.5^\circ \text{ C}$ . Strains were determined by an Instron electrical strain gage extensometer with a sensitivity of about 0.1%. In most cases, tests were run up to ultimate failure. Rupture surfaces were examined by scanning microscopy.

A few relaxation tests were performed on resin mix 60/40 at different temperature levels.

### Test Results and Discussion

Strain-rate and temperature variations were found to affect strongly the mechanical behavior of the epoxy resins. The influence of these factors on the following characteristics were studied:

- a. stress-strain (S.S.) relationship
- b. mode of failure
- c. yield and ultimate stress and strain
- d. tangent and relaxation moduli

a. The shape of S.S. curve changed significantly with temperature above  $5^\circ \text{ C}$ . A monotonously increasing curve up to failure was typical at temperatures below room temperature (Figure 1a). At intermediate temperatures (R.T. to about  $40^\circ \text{ C}$ ), S.S. curve was characterized by a maximum stress plateau followed by reversal of slope and failure at lower stress levels (Figure 1b). At somewhat higher temperatures, the S.S. curve shows a secondary lower plateau followed by a stress increase (similar to strain-hardening effects in metals) up to failure (Figure 1c). At still higher temperatures (above  $60^\circ \text{ C}$ ), a typical rubbery stress-strain relationship was found, with no

apparent stress plateau and a monotonously increasing curve up to failure (Figure 1d). There was no clear-cut shift from one mode to the other, and in a few cases failure occurred at the middle of the higher or lower stress plateau. Similar variations in stress-strain relationships were affected to a lesser extent by the strain rate; mode 1a was typical to extremely high and 1d to extremely low strain rates at moderate temperatures.

b. Failure mode was affected by temperature and strain rate in parallel with S.S. characteristics. Brittle failure mode prevails at low temperatures and high strain rates in correspondence with S.S. mode 1a. Macro-observation of the rupture area revealed almost no permanent distortion and a considerable roughness at the rupture surface originated from a single point origin (Figures 2a, 3a), which is typical of a brittle mechanism associated with fast crack propagation. A lower ultimate stress value and high scatter characterize the brittle failure mode in comparison to the good reproducibility of data found in case of ductile behavior. A ductile failure mode associated with S.S. curve of Figure 1b was found to prevail at moderate temperature and strain-rate regions. Rupture plane in this case was found to consist of small smooth area indicating probably a slow crack propagation, and a major finely rough portion showing an oriented pattern\* (Figure 2b). Ductile failure mode was associated with pronounced local necking and plastic deformations, and glide lines at about  $45^\circ$  to the tensile axis were observed on the surface (Figure 3b).

---

\*Similar morphological pattern is generally observed in tensile rupture of glassy polymers [19]. The boundary between the smooth and rough surfaces is regarded as a transition between subcritical and critical crack growth [20].

The rubbery behavior represented by the S.S. mode of Figure 1d was associated with slow crack propagation process distributed all over the gage-length (Figure 3c). Eventually at a strain level of above 30% (in extreme cases) a separation at one location occurred. Observation at rupture surface revealed a smooth area over the entire cross-section (Figure 2c).

The dependence of failure modes on temperature and strain-rate variables and the transition from one mode to the other could be defined more clearly by mapping the three basic modes on a temperature vs. strain rate coordinates (Figures 4a, 4b). Brittle, ductile and rubbery failure are designated by B, D and R, respectively. The transitions from the ductile into brittle and rubber modes are located on two continuous temperature log strain-rate curves. Ductile behavior seems to be confined within a narrow temperature range of about 35° C, extending from 15° to 50° C and from 25° to 65° C in cases of 60/40 and 70/30 mixes, respectively. The full bounds for the ductile failure could not be established owing to a relatively small strain-rate range. It could be assumed, however, that ductile behavior could be defined within a closed region located on the temperature-strain-rate plane. This ductile region is bounded by the brittle and rubbery regions which extend from its lower right side and higher left side, respectively. It could be concluded that the epoxy-versamid systems would reveal all three failure modes, the prevailing one of which depends on the specific temperature and strain-rate. The relatively small ductile region found in the present case is believed to be typical to the present cross-linked material. A broader ductile region was found [15-21] and is expected in case of linear polymers such as P.M.M.A. at their glassy-leathery-rubbery transition.

c. Yield stress  $\sigma_y$  and strain  $\epsilon_y$  values were obtained from stress-strain curves such as those shown in Figure 5. Plots of  $\sigma_y$  vs.  $\log \dot{\epsilon}$  at different temperatures (Figures 6a, 6b) give a linear relation in the ductile region (defined in Figure 4). Yield stress decreases with increasing temperature. The unclear trend of  $\sigma_y$  vs.  $\log \dot{\epsilon}$  is manifested above 60° C for the 60/40 mix and above 75° for the 70/30 mix, which is consistent with the ductile-rubbery transitions in failure mode occurring at these levels. The slopes of most plots seem to be common at all temperature levels of ductile region. Slightly lower slopes and higher yield levels are evident for the 70/30 mix (Figure 6b).

Yield strain is defined here according to previous works [11, 16] as the strain at the end of the yield plateau where the slope is reversed (Figure 1b). Plots of  $\epsilon_y$  vs.  $\log \dot{\epsilon}$  at different temperatures (Figure 7) indicate that yield strain (as defined above) is almost invariant with strain rate but decreases slightly with a temperature rise. Yield strain for the present work could be established to be in the order of 5%  $\pm$  0.5%. The extremely higher and lower points and the scatter shown in Figure 7 is reasonably within the expected experimental error. The fluctuation of  $\pm 0.5\%$  in yield strain is negligible compared to the variation in yield stress and elastic modulus which was found to decrease by an order of magnitude over the temperature and strain-rate range covered in this study. The characteristics of yield strain and its values are in agreement with recent data given by Tobolsky, et al., which suggest direct relationship between yield strain and the average free volume of the polymer [22-24].

d. Young's modulus ( $E_0$ ), defined as the initial slope, was derived from the S.S. curves of Figure 5. Plots of  $E_0$  vs. temperature for the 60/40 mix at three strain-rate levels are shown in Figure 8. Two different trends could be distinguished. A moderate modulus decrease with temperature prevails below R.T., followed by a steep fall at higher temperature levels down to about 10% of its R.T. value at 66° C. Strain rate has a minor effect manifested by upward shift of the modulus-temperature curve at higher rates. The abrupt change in slope may serve to indicate for the glass transition of the system, which seems to occur at room temperature (about 28° C for the 60/40 mix and probably slightly above 28° C for the 70/30 mix) (Figure 9). The tensile relaxation modulus ( $E_t$ ) was evaluated from tests at constant strain levels ranging from 0.25% to 1%. Stress values were determined over a 10-minute period. Relaxation curves of different temperatures are shown in Figure 10 for 60/40 mix. The extent of linear viscoelasticity (i.e., the proportionality of stress to initial strain in this case) was found to prevail below strain level of 0.75%. Plots of  $E_t$  vs. temperature for different time periods show a trend similar to that of tangent modulus  $E_0$  (Figure 9). The present work is concerned mainly with yield and failure characteristics; thus, no further attempt was pursued in this direction. It has to be pointed out, however, that time-temperature shift techniques were found to be applicable for the linear viscoelastic data of different epoxy systems at their transition region [25, 26].

### Analysis of Results

Three approaches could be applied for interpretation of time-temperature mechanical data:

- a. The rate process theory of Eyring.
- b. The semi-empirical time-temperature reduction technique.  
(represented by the W. L. F. Equation.)
- c. A macro-rheological relationship to relate stress to strain rate and temperature by introducing constant material parameters.

Plots of yield stress vs. temperature for constant strain rate levels (Figure 11) together with the isotherms shown in Figure 6, indicate that the simplified Eyring's equation would hold for the ductile region. It could be formulated in the following way:

$$\dot{\epsilon} = [AT] \exp [-Q/RT] \exp [V_0 \sigma / 4KT] \quad (1)$$

- where
- $\dot{\epsilon}$  = strain rate
  - $\sigma$  = normal flow stress
  - $T$  = absolute temperature
  - $A$  =  $K/h$  - rate-process parameter
  - $K$  = Boltzman constant
  - $h$  = Planck's constant
  - $Q$  = "apparent activation energy"
  - $R$  = universal gas constant
  - $V_0$  =  $\lambda_1 \lambda_2 \lambda_0$  - activation volume\*
  - $\lambda_1, \lambda_2$  = longitudinal and transverse dimensional units of the activated molecular segment, respectively
  - $\lambda_0$  = jump distance

---

\*The parameter  $V_0$  may be regarded as a measure of the activated segmental unit involved in the diffusional process [27].

The constants  $A$ ,  $Q$ , and  $V_0$  are considered as the three basic material parameters of the process. The assumption, supported by the data, is that they are independent of stress, strain-rate, and temperature.

The term  $[AT]$  was found to be relatively insensitive to temperature within the ductile region for the present case. Equation (1) could thus be written as follows:

$$\log \dot{\epsilon} = A_0 - A_1/T + A_2\sigma/T \quad (2)$$

$$\text{and} \quad A_0 = \log [AT] ; \quad A_1 = Q \log e/R$$

$$A_2 = V_0 \log e/4K$$

where  $A_0$ ,  $A_1$ , and  $A_2$  are assumed to be parameters independent of stress, temperature, and time variables. The isothermic state could be formulated as follows:

$$\log \dot{\epsilon} = B_0 + B_1\sigma \quad (3)$$

$$\text{and} \quad B_0 = A_0 - A_1/T$$

$$B_1 = A_2/T$$

where  $B_0$  and  $B_1$  are temperature-dependent parameters. The activation volume could be derived from the isotherm slopes. The isochrones shown in Figure 11 would be represented by the following relationship:

$$\sigma = C_1 T - C_0 \quad (4)$$

$$\text{where} \quad C_1 = [\log \dot{\epsilon} - A_0] / A_2$$

$C_0 = A_1/A_2$  and  $C_1$  is strain-rate dependent. The "apparent activation energy" and the  $A$  parameter could be evaluated directly by the use of Equation (4).

The general Equation (1) and its three versions seem to hold reasonably well for the two mixes within the ductile region as defined in this work. The computed values of the parameters  $A_0$ ,  $A_1$ ,  $A_2$ ,  $Q$  and  $V_0$  have been derived from the experimental data and are given in Table I. The real physical significance of the activation energy at the glassy and transition region is quite questionable. Data and discussion by Bueche (27) and others (28) show that this parameter is relatively high and is strongly dependent on temperature at this region. It was concluded that the so-called "apparent activation energy" could not be related to binding energy barriers as is usually interpreted in case of Newtonian viscous flow. The invariance of  $Q$  in the ductile region, however, is evident in the present case. Its value seems to be up above the Van der Waal's and hydrogen secondary binding energy levels, and below that of the expected primary binding of the system. The effect of the versamid content in the resin is insignificant on the  $Q$  and  $A$  values but seems to influence the activation-volume parameter. This is attributable to morphological changes within the internal structure occurring by increasing the amount of the versamid "plasticizer" groups in the copolymeric system.

This trend is also reflected by the consistent increase of the mechanical yield and modulus variable with the decrease of versamid content as shown clearly in Figure 12. The data for 50/50 mix was taken from Reference 11.

A macro-rheological approach could be based on the yield stress as the primary variable and Equation (2) could be transformed as follows:



TABLE I

PHYSICAL MATERIAL PARAMETERS WHICH CHARACTERIZE  
THE YIELD PROCESS OF TWO EPOXY-VERSAMID MIXES

	60/40	70/30
$A_0$	34	35
$A_1$ deg.	12500	13500
$A_2$ deg. cm <sup>2</sup> /kg	3.80	4.65
$V_0$ [Å] <sup>3</sup>	4800	5800
$Q$ kcal/mole	58	62

$$\sigma_y = D_0 + D_1 T \log \dot{\epsilon} - D_2 T \quad (5)$$

where  $D_0 = A_1/A_2$  ;  $D_1 = 1/A_2$  ;  $D_2 = A_0/A_2$

The D values, which are assumed to be rheological parameters independent of stress, time and temperature, are given in Table 2.

Equation (5), in analogy with the basic elastic and viscoelastic constituent equations, is considered to be more adequate for further mathematical-mechanical analysis, as well as for prediction of yield stress in more practical applications. The general relationship between yield stress, log strain rate and temperature could be described geometrically as a limiting yield surface on a three-dimensional coordinate system. It could also be projected on the  $\sigma_y - \log \dot{\epsilon}$  plane by applying time-temperature shift analysis, similar to the work done by Smith (29) and others on tensile failure of rubbery polymers. The first representation would give a planar surface at the ductile zone, where the second would lead probably to a linear master plot at this region.

### Conclusions

Loading of tensile epoxy-versamid specimens up to failure were conducted under different C.S.R. and temperature levels at the range of  $5 \times 10^{-4} - 0.5 \text{ min}^{-1}$  and  $5^\circ \text{C} - 75^\circ \text{C}$  respectively. Analysis of results leads to the following conclusions:

1. The mechanical behavior of the above systems, which is assumed to be representative of other plasticized cross-linked polymers at their glassy

TABLE II  
RHEOLOGICAL PARAMETERS OF EQUATION (5) FOR THE TWO EPOXY-VERSAMID MIXES

	Unit	60/40	70/30	Unit	60/40	70/30
$D_0$	k. s. i.	40200	40400	$\text{kg/cm}^2$	3300	2980
$D_1$	k. s. i. / $1^\circ \text{C}$	3.67	3.01	$\text{kg/cm}^2 1^\circ \text{C}$	0.26	0.215
$D_2$	k. s. i. / $1^\circ \text{C}$	126	105	$\text{kg/cm}^2 1^\circ \text{C}$	9.00	7.52

and transition regions, reveal three failure modes, namely: brittle, ductile and rubbery. The prevailing specific mode is dependent on strain-rate and temperature coordinates involved.

2. The ductile zone is located within a narrow band on the  $T - \log \dot{\epsilon}$  plane extended approximately from 15° to 50° C and from 25° to 65° C in cases of 60/40 and 70/30 mixes, respectively. It is bounded by the rubbery and the brittle zones on its upper and lower ends, respectively.
3. The specific nature of the ductile mode of behavior is also revealed by the pronounced yield plateau of the S.S. curves, the linear dependence of yield-stress on log strain-rate and temperature, and by the modulus-temperature relationship.
4. Yield strain seems to be almost unaffected by time and decreases slightly with temperature rise, compared to the strong influence of these variables on yield-stress and modulus.
5. Analysis indicates that yield-stress characteristics within the ductile zone could be well formulated by Eyring's equation. This leads to the evaluation of "apparent activation energy" and activation volume for the two epoxy mixes.
6. Comparison with other data indicates that the increase of versamid content in the system tends to decrease the activation volume parameter as well as the level of yield stress and modulus variables. This is consistent with attributing the plasticification role to the versamid sub-structure within the resin system.

7. The analysis provides also a simple formulation for direct prediction of yield stress. It could be concluded, for more practical purposes, that the epoxy-versamid system, while showing good performance at room temperature and below, becomes less stable above it. This is reflected by the pronounced decrease of both ultimate-stress and modulus with temperature rise and their strong dependence on strain-rate.

#### Acknowledgments

The author wishes to express his gratitude to Dr. J. C. Halpin for his valuable comments, to Mr. R. L. Thomas for his assistance in the experiments, to Messrs. C. N. Rasnick and J. J. Cornell for their help in the fabrication of specimens, and to Mr. W. Renaudette for the photographic and scanning microscopy part of the work.

This work was sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research, Contract No. N00014-67-C-0218.

## REFERENCES

1. J. S. Lazurkin, J. Polymer Sci., 30 (1958), p. 595.
2. R. E. Robertson, J. Appl. Polymer Sci., 7 (1963), p. 443.
3. C. B. Arends, J. Appl. Polymer Sci., 10 (1966), p. 1099.
4. H. Eyring, J. Chem. Phys., 4 (1936), p. 283.
5. J. A. Sauer and J. Marin, J. Appl. Phys., 20 (1949), p. 507.
6. C. C. Hsiao and J. A. Sauer, ASTM Bull., 172 (1951), p. 29.
7. R. G. Cheatham and A. G. H. Dietz, Trans. ASME, 74 (1952), p. 31.
8. D. A. Zaukelies, J. Appl. Phys., 33 (1962), p. 2797.
9. M. F. Bender and M. L. Williams, J. Appl. Phys., 34 (1963), p. 3329.
10. C. J. Speerschnider and C. H. Li, J. Appl. Phys., 34 (1963), p. 3004.
11. O. Ishai, J. Appl. Polymer Sci., 11 (1967), p. 963.
12. F. Bueche, J. Appl. Phys., 28 (1957), p. 784.
13. T. L. Smith, J. Polymer Sci., 32 (1958), p. 99.
14. T. L. Smith, J. Appl. Phys., 31 (1960), p. 1892.
15. J. J. Lohr, Trans. of the Soc. Rheology, 9 (1965), p. 65.
16. O. Ishai, J. Appl. Polymer Sci., 11 (1967), p. 1863.
17. I. Steg, O. Ishai, J. Polymer Sci., 11 (1967), p. 2303.
18. O. Ishai, R. Anderson and R. Lavengood, "Failure-time Characteristics of Unidirectional Continuous Glass-Epoxy Composites in Flexure," Monsanto/Washington University ONR/ARPA Association Interim Report, December 1967.
19. I. J. Leeuwrik, Rheologica Acta, 2 (1962), p. 10.
20. A. S. Tetelman and A. J. McEvily, Fracture of Structural Materials, Wiley (1967), p. 619.

21. R. E. Robertson, "An Equation for the Yield Stress of a Glassy Polymer," G. E. Technical Information Series, Report No. 67-C-353, presented at the ACS meeting, September 1967.
22. M. H. Litt and A. V. Tobolsky, J. Macromol. Sci., B1(3), (1967), p. 587.
23. M. H. Litt and P. Koch, Polymer Letters, 5 (1967), p. 251.
24. M. H. Litt, P. J. Koch, and A. V. Tobolsky, J. Macromol. Sci., B1(3) (1967), p. 587.
25. P. S. Theocaris, Rheologica Acta, 2 (1962), p. 92.
26. P. S. Theocaris and Chr. Hadji:oseph, Proceeding of the 4th Int. Congress on Rheology, Interscience, New York (1965), p. 485.
27. F. Bueche, Physical Properties of Polymers, Interscience Publishers, Wiley (1962), p. 91.
28. J. McLoughlin and A. V. Tobolsky, J. Polymer Sci., 8 (1952), p. 543.
29. T. L. Smith, J. Appl. Phys., 35 (1964), p. 27.

## FIGURE CAPTIONS

- Figure 1 Typical stress-strain curves representing the different modes of behavior up to yield and failure of epoxy-versamid system.
- Figure 2 Scanning microscopy pictures of rupture-surfaces typical for the three following failure modes: 2a - brittle, 2b - ductile, 2c - rubbery. (X15)
- Figure 3 Pictures of tensile epoxy specimens near the rupture location, typical for the three following failure modes: 3a - brittle, 3b - ductile, 3c - rubbery. (X28)
- Figure 4 The tensile failure modes of epoxy-versamid specimens as located on the temperature-strain rate plane, in case of 60/40 mix (4a) and 70/30 mix (4b).
- Figure 5 Typical tensile stress-strain curves under different constant strain rates at constant temperatures for 60/40 epoxy-versamid resin.
- Figure 6 The dependence of yield stress on strain rate at different isothermic temperature levels for epoxy-versamid systems of 60/40 mix (6a) and 70/30 mix (6b).
- Figure 7 The dependence of yield strain on strain rate at different temperature levels for epoxy-versamid systems of 60/40 mix (7a) and 70/30 mix (7b).
- Figure 8 The dependence of tensile tangent modulus on temperature under different C.S.R. levels for 60/40 epoxy-versamid mix.
- Figure 9 The dependence of tangent and relaxation moduli on temperature for the two epoxy-versamid mixes.
- Figure 10 Typical relaxation modulus vs. time at different temperature levels for the 60/40 epoxy-versamid mix.
- Figure 11 The dependence of yield stress on temperature under different C.S.R. levels for the epoxy-versamid systems of 60/40 mix (11a) and 70/30 mix (11b).
- Figure 12 The effect of versamid content in the epoxy resin on the activation volume and mechanical characteristics at room temperature.



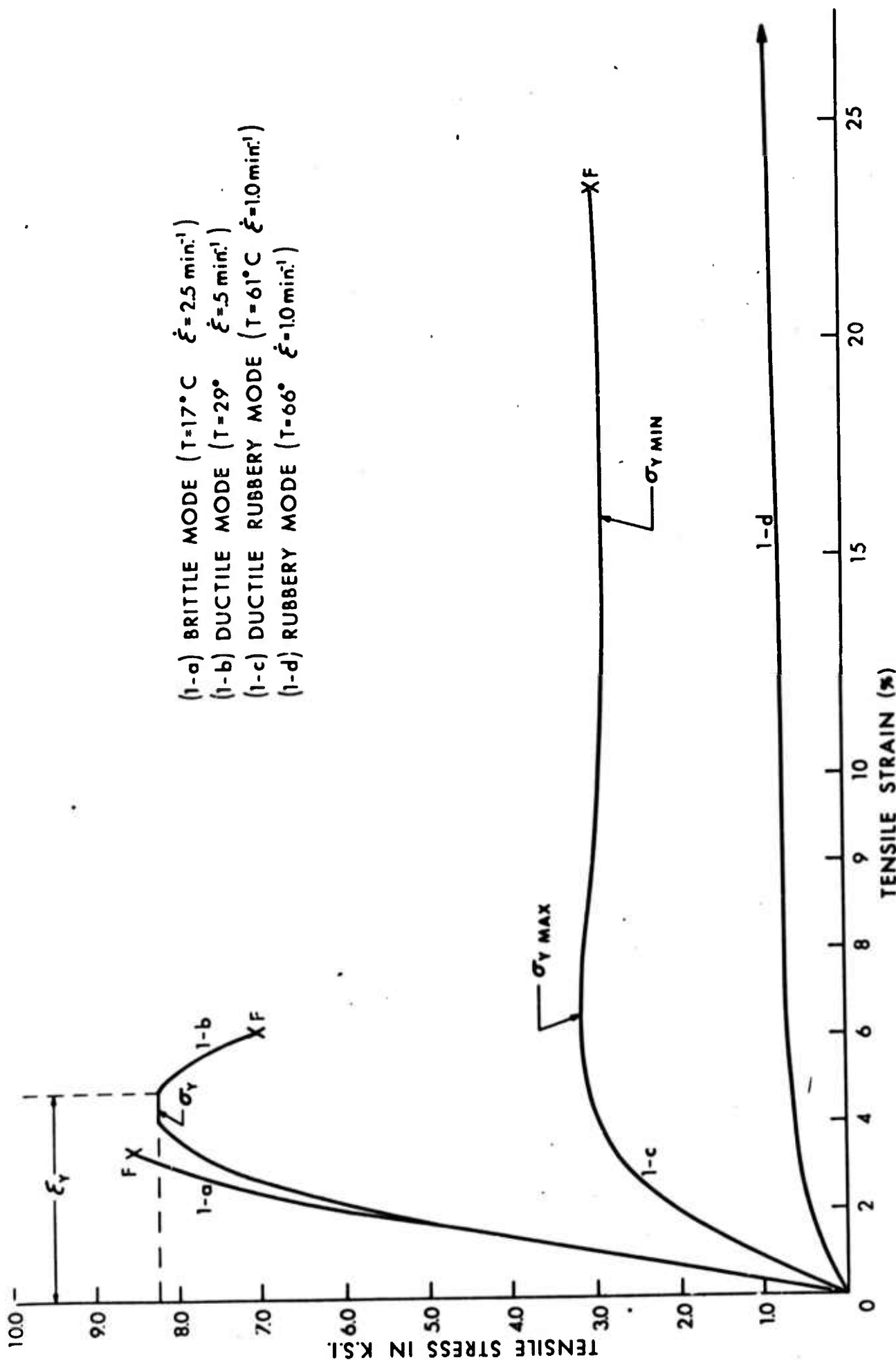


FIGURE 1 TYPICAL STRESS-STRAIN CURVES REPRESENTING THE DIFFERENT MODES OF BEHAVIOR UP TO YIELD AND FAILURE OF EPOXY-VENISAND SYSTEM.

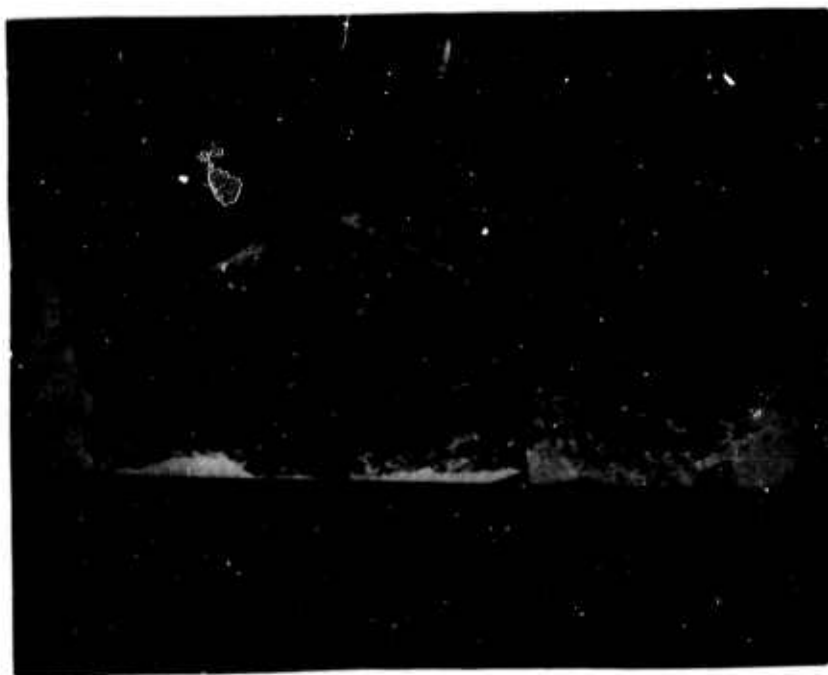


Figure 2a

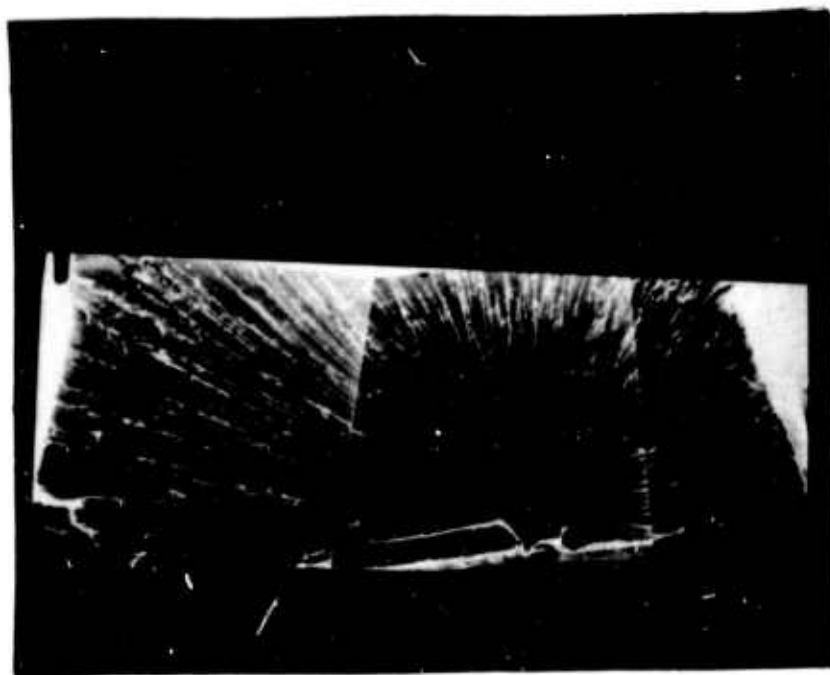


Figure 2b

Scanning microscopy pictures of rupture-surfaces typical for the following failure modes: 2a - brittle; 2b - ductile.

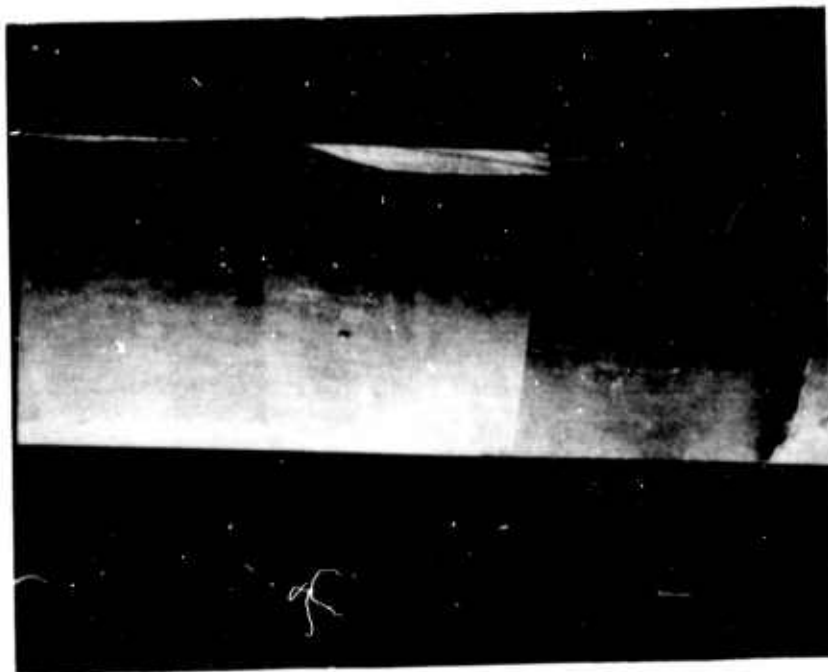


Figure 2c

Scanning microscopy pictures of rupture-surfaces typical for the following failure mode: rubbery. (X15)



Fig. 3a

3b

3c

Pictures of tensile epoxy specimens near the rupture location, typical for the three following failure modes: 3a - brittle; 3b - ductile; 3c - rubbery. (X28)

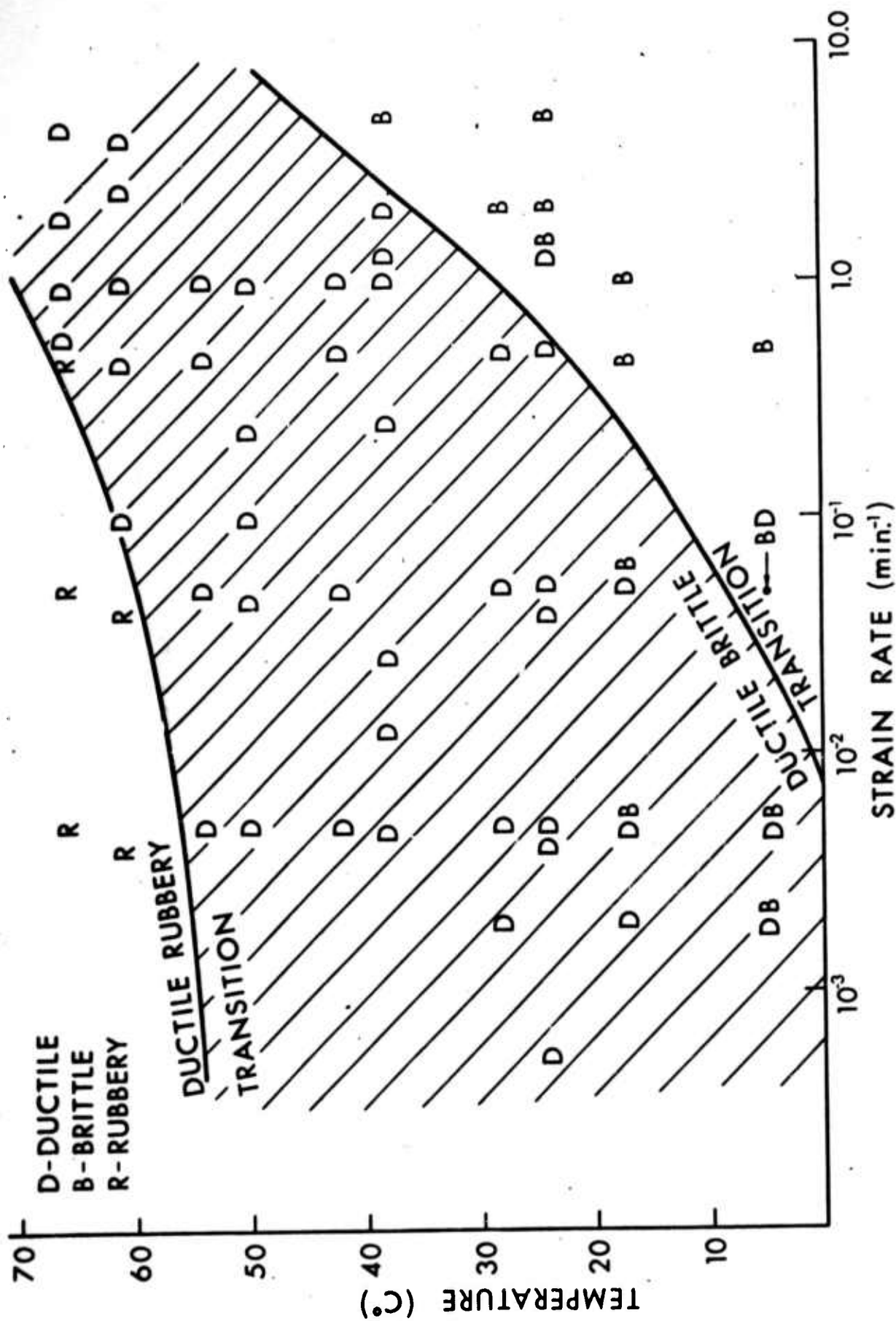


Fig. 4a. The tensile failure modes of epoxy-versamid specimens as located on the temperature-strain rate plane in case of 60/40 mix.

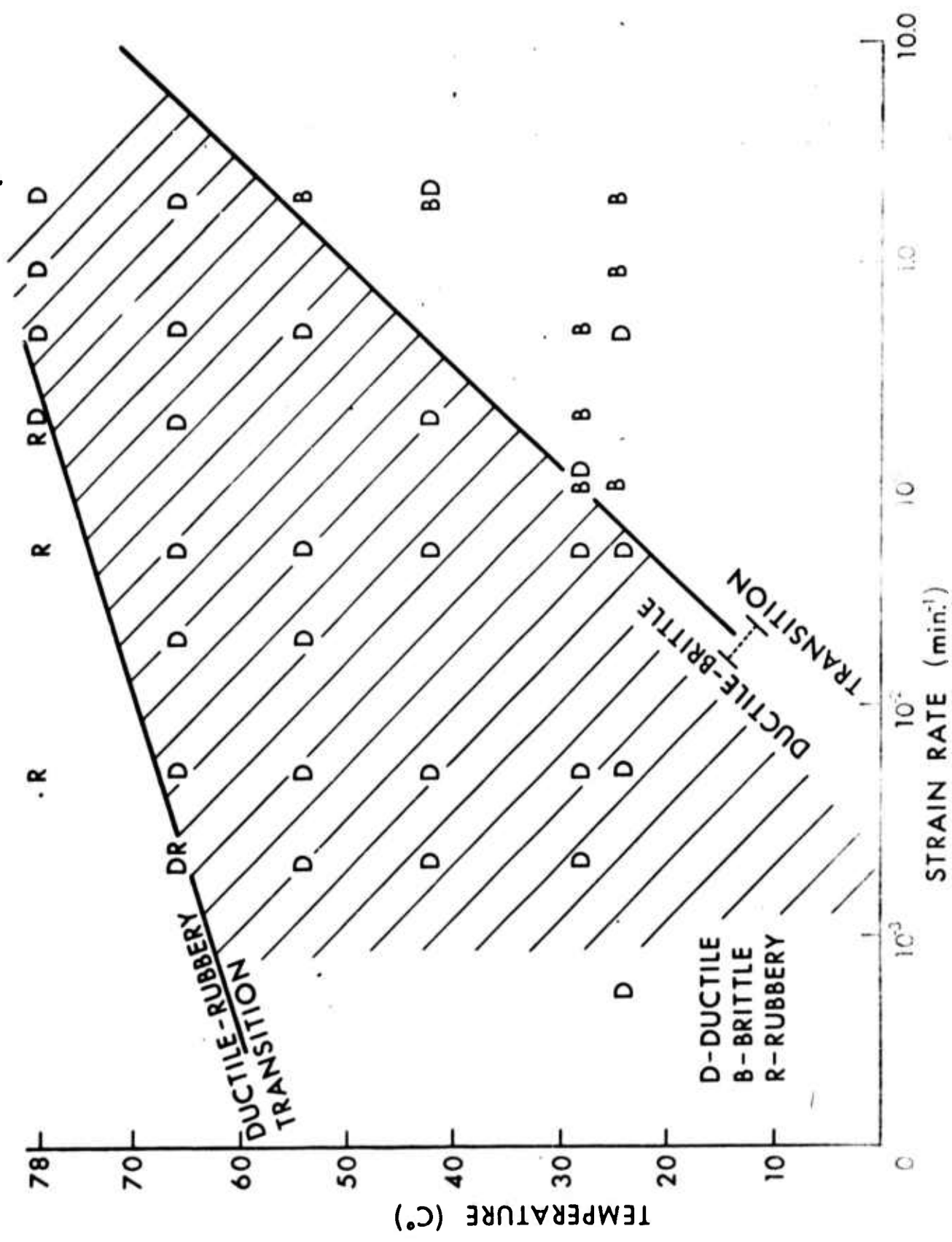


FIGURE 43 THE TENSILE FAILURE MODES OF EPOXY-VERSAND SPECIMENS AS LOCATED ON THE TEMPERATURE-STRAIN RATE PLANE IN CASE OF 70/30 MTY

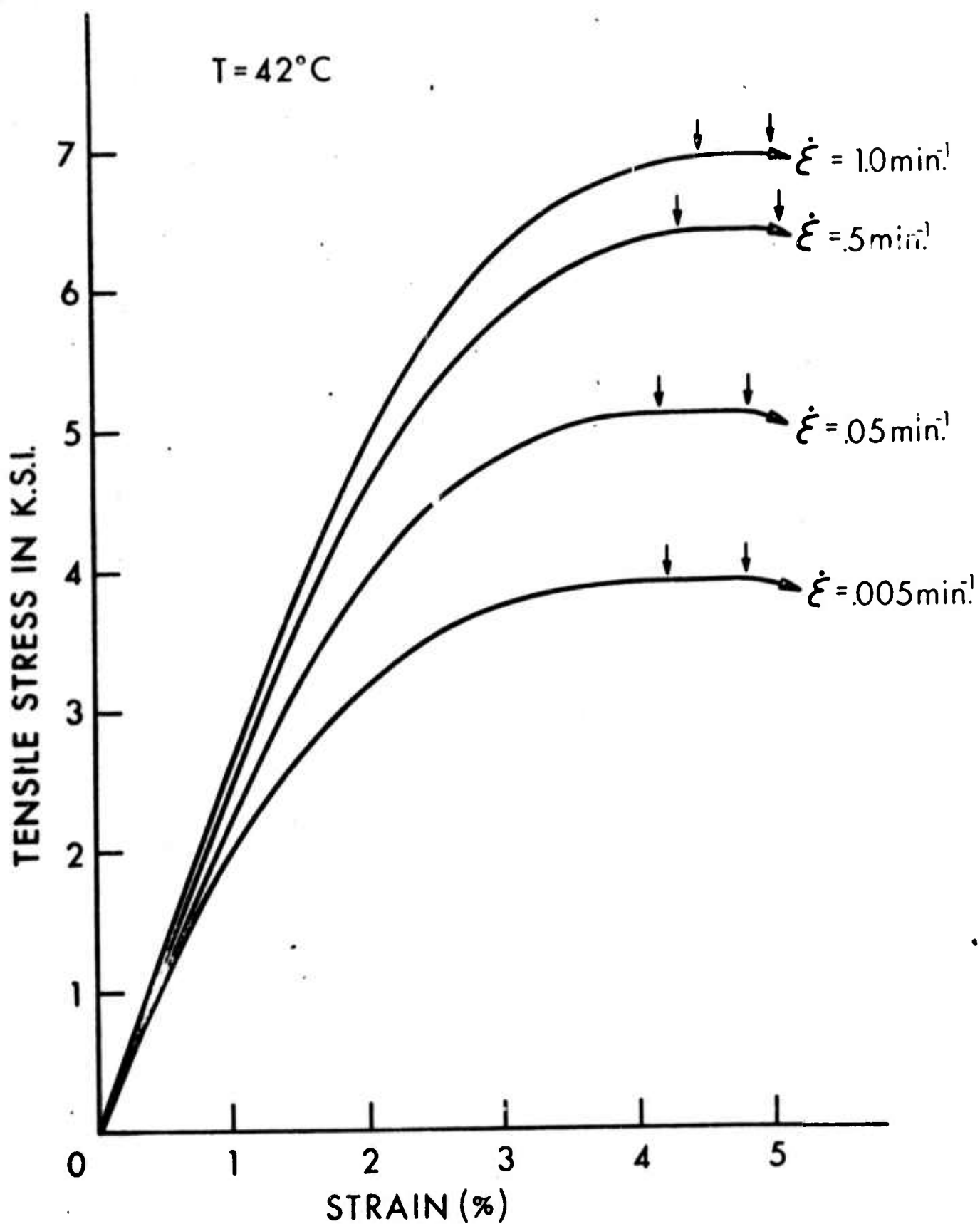


Figure 5 Typical Tensile Stress Strain Curves Under Different Constant Strain Rates for 60/40 Epoxy-Versamid Resin [at a Temperature of  $42^{\circ}$ ].

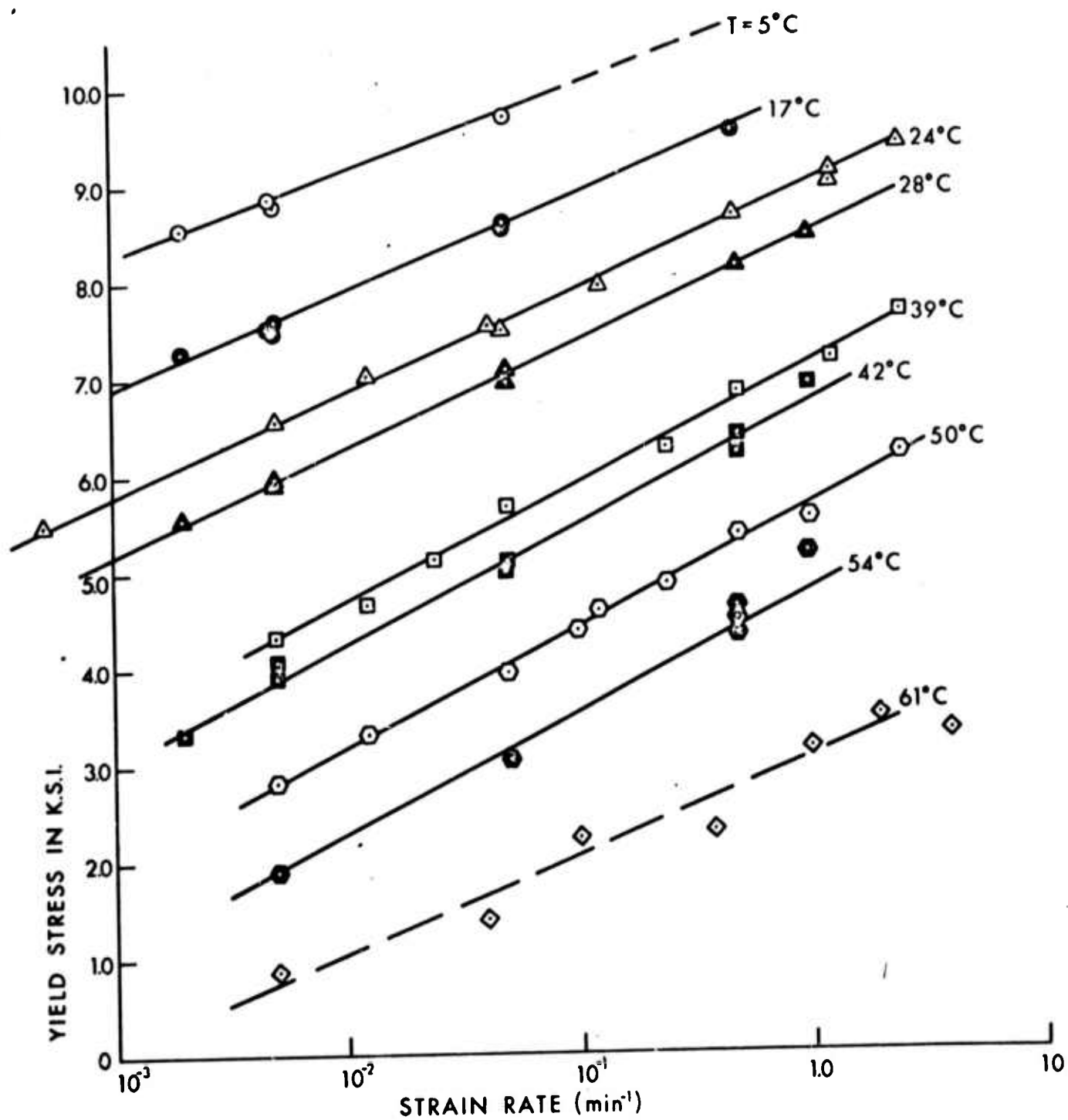


FIGURE 6A THE DEPENDENCE OF YIELD STRESS ON STRAIN RATE AT DIFFERENT ISOTHERMIC TEMPERATURE LEVELS FOR EPOXY-VERSAMID SYSTEMS OF 60/40 MIX.

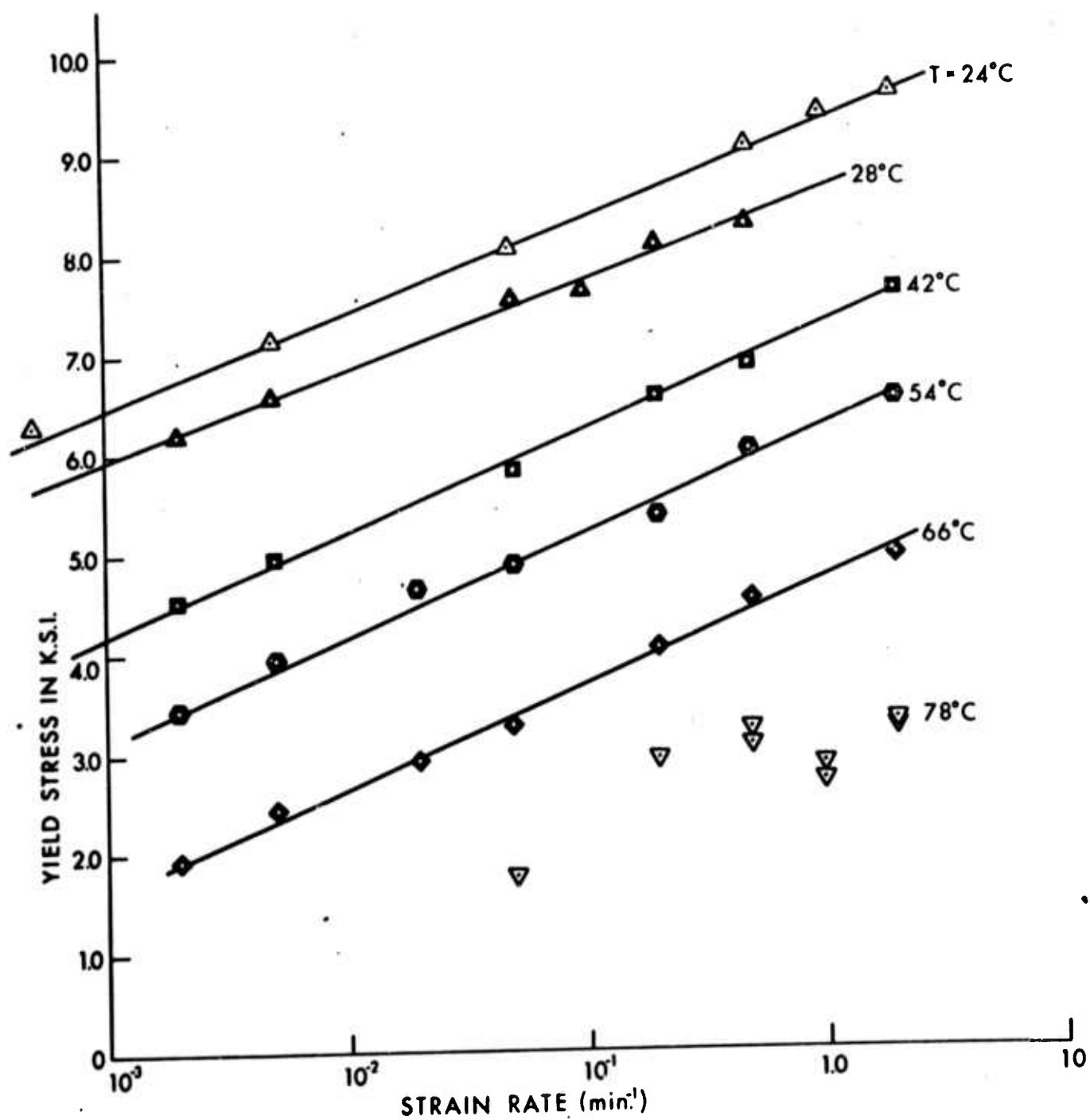


FIGURE 6B THE DEPENDENCE OF YIELD STRESS ON STRAIN RATE AT DIFFERENT ISOTHERMIC TEMPERATURE LEVELS FOR EPOXY-VERSACID SYSTEMS OF 70/30 MIX.



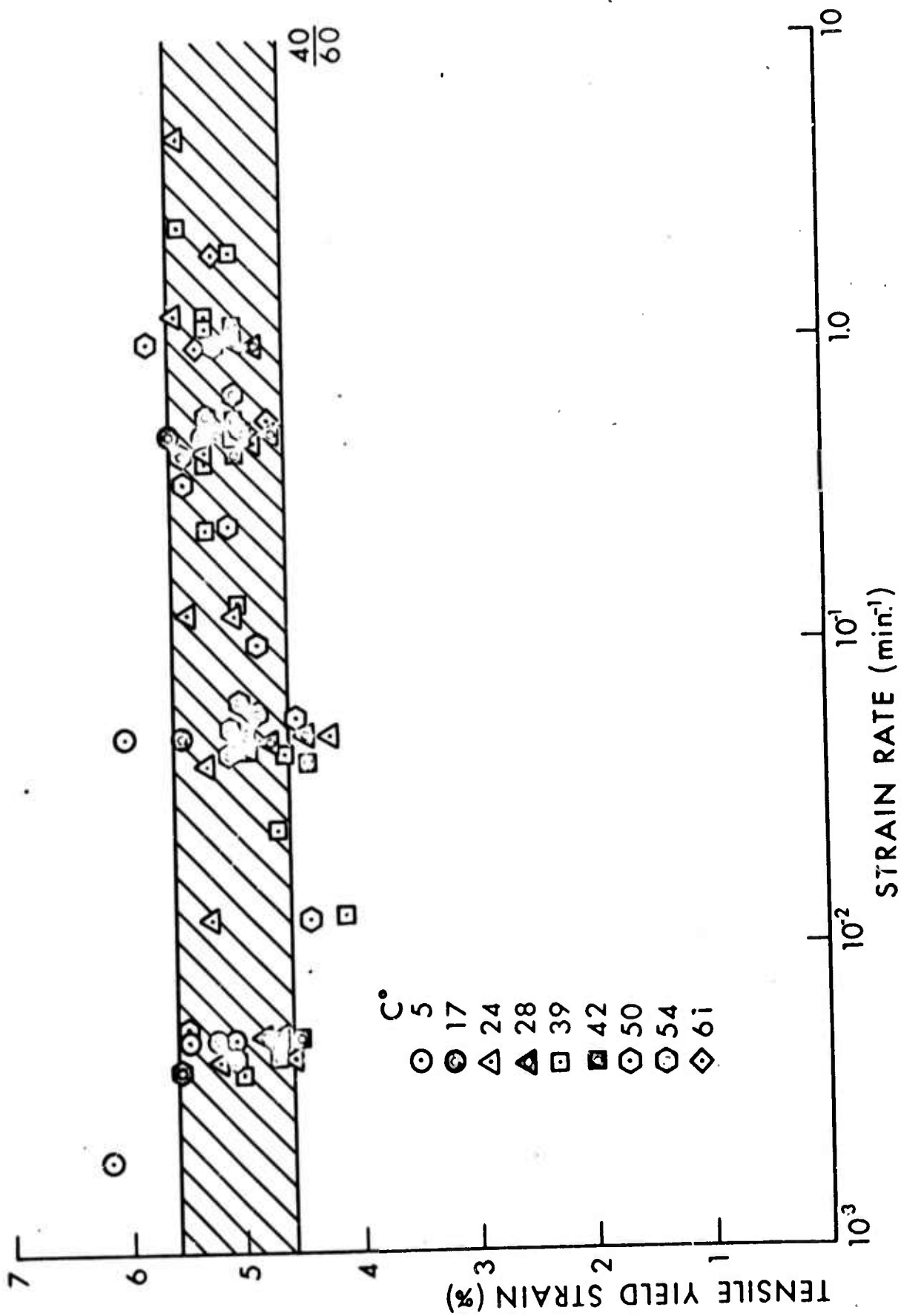


FIGURE 7A THE DEPENDENCE OF YIELD STRAIN ON STRAIN RATE AT DIFFERENT TEMPERATURE LEVELS FOR THE EPOXY-VERSAMID SYSTEMS OF 60/40 MIX.

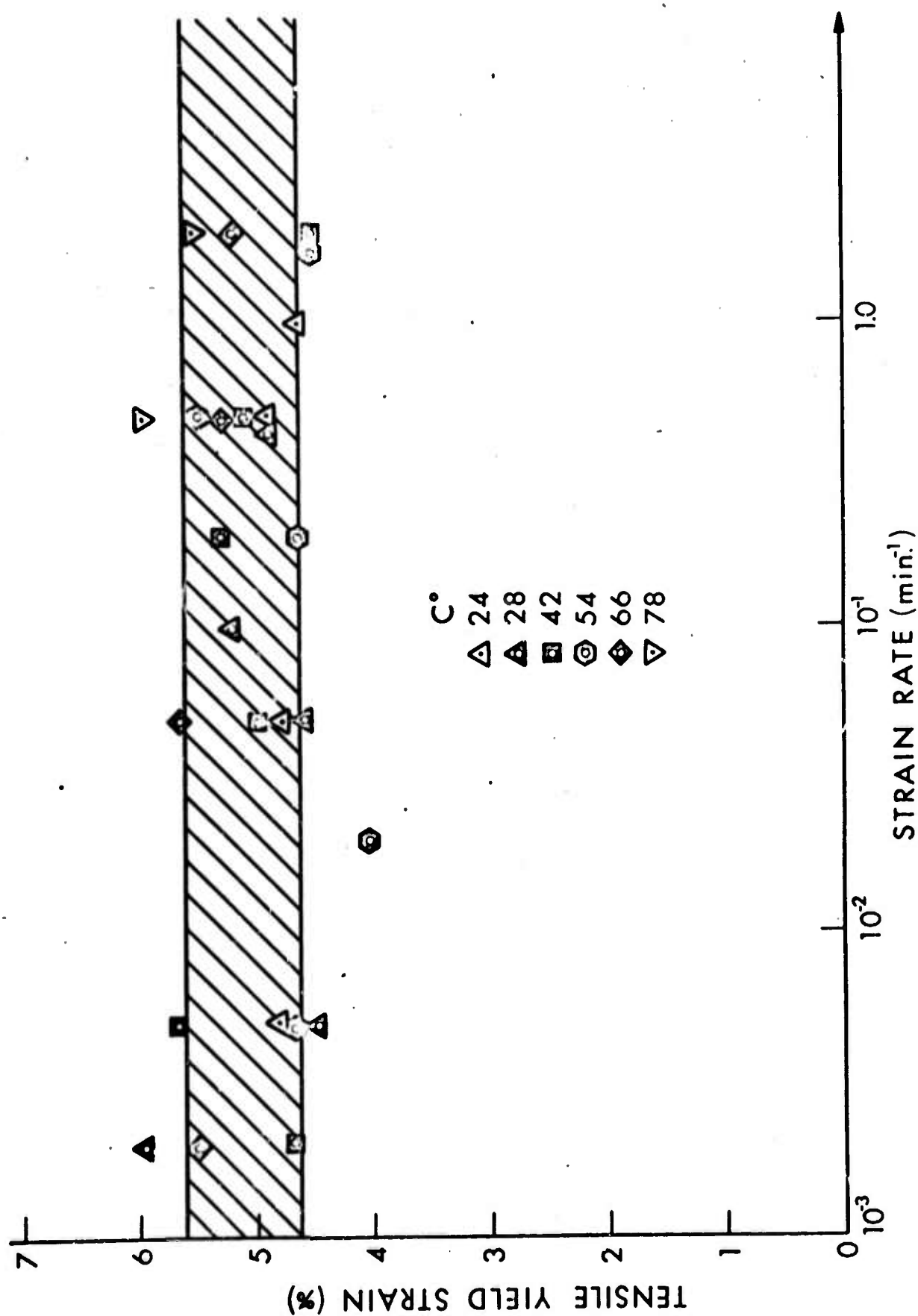


FIGURE 7B THE DEPENDENCE OF YIELD STRAIN ON STRAIN RATE AT DIFFERENT TEMPERATURE LEVELS FOR THE EPOXY-VERSAMID SYSTEMS OF 70/30 MIX.

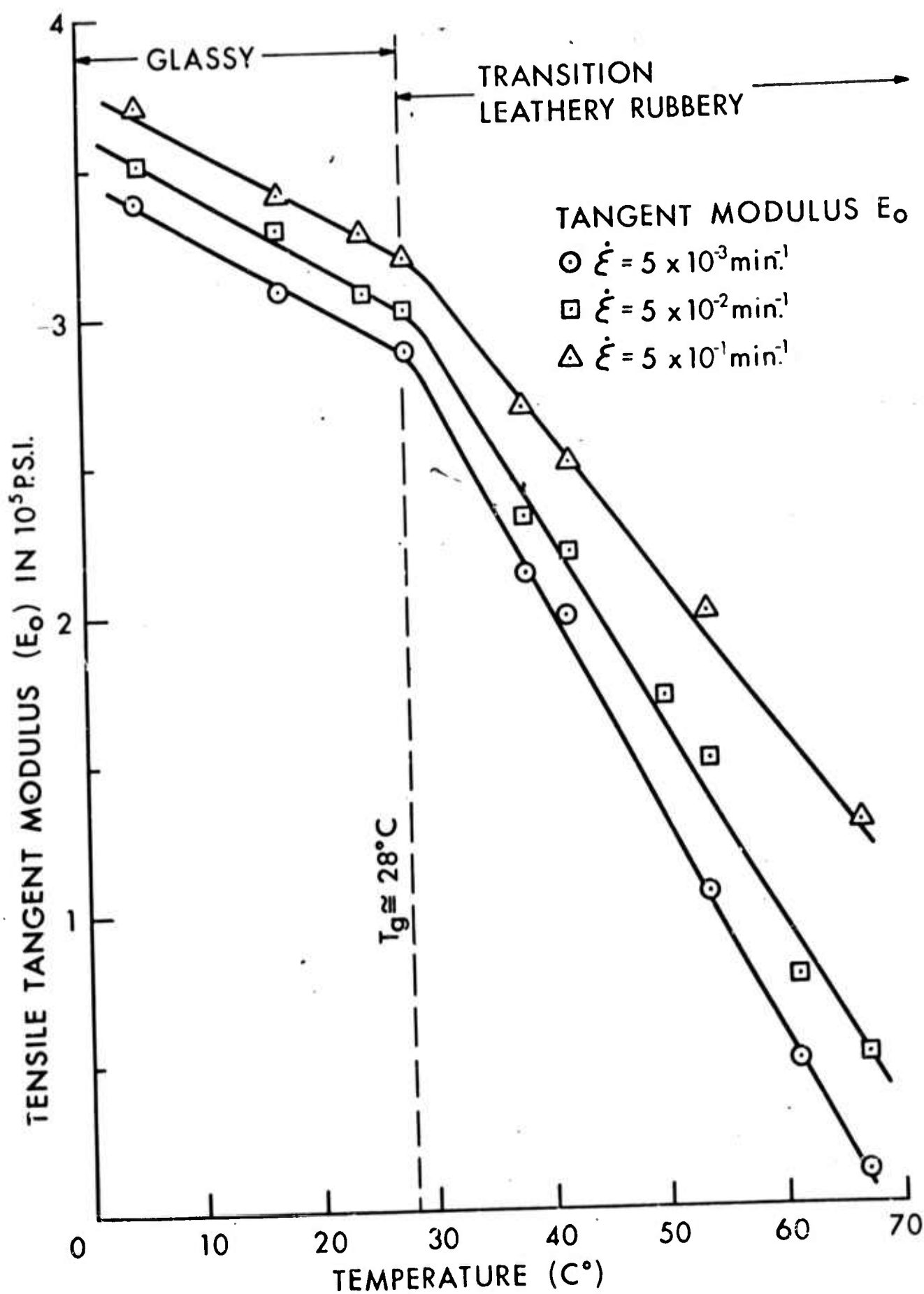


FIGURE 8 THE DEPENDENCE OF TENSILE TANGENT MODULUS ON TEMPERATURE UNDER DIFFERENT C.S.R. LEVELS FOR 60/40 MIX.

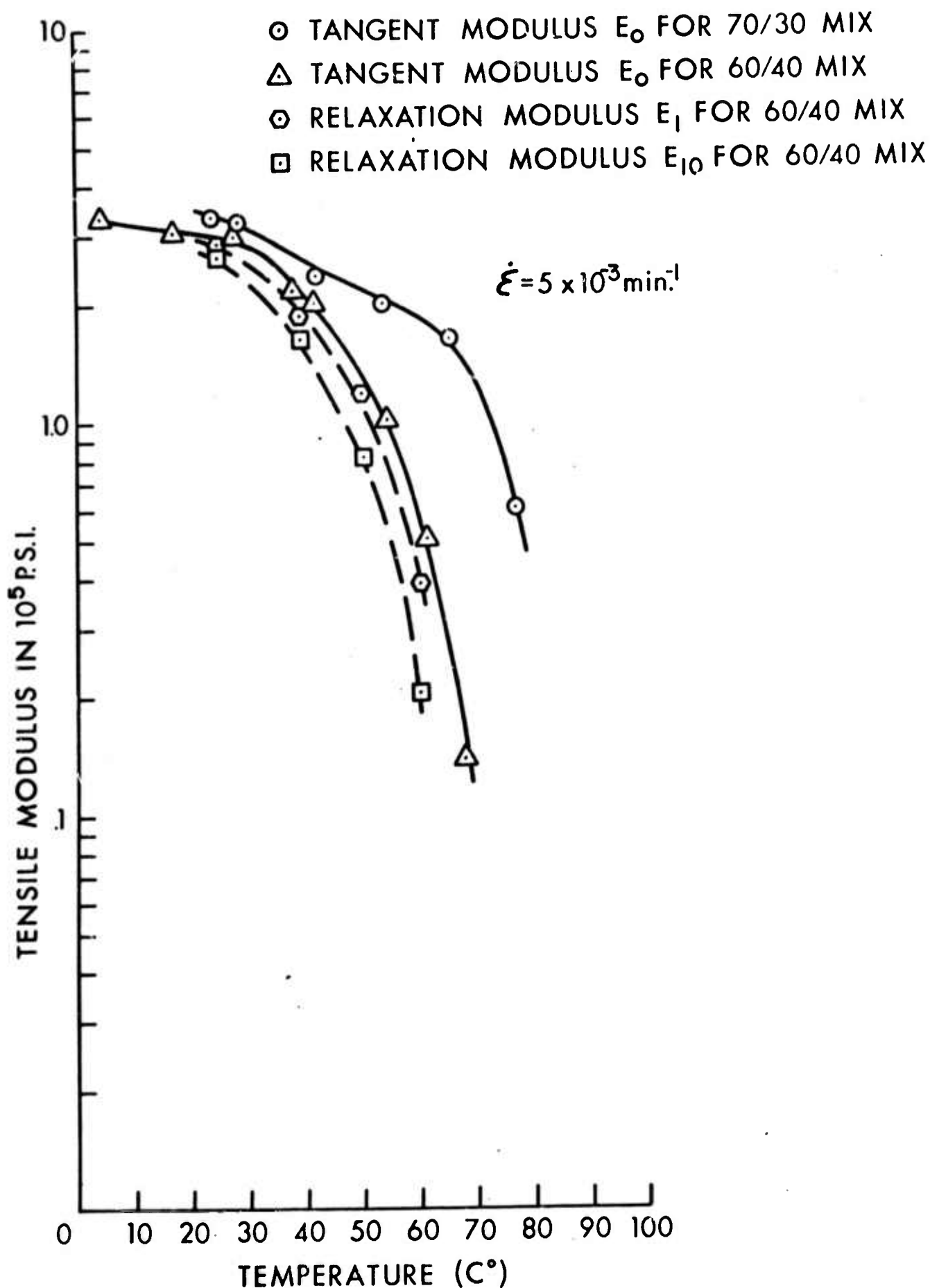


FIGURE 9 THE DEPENDENCE OF TANGENT AND RELAXATION MODULI ON TEMPERATURE FOR THE TWO EPOXY-VERSAMID MIXES.

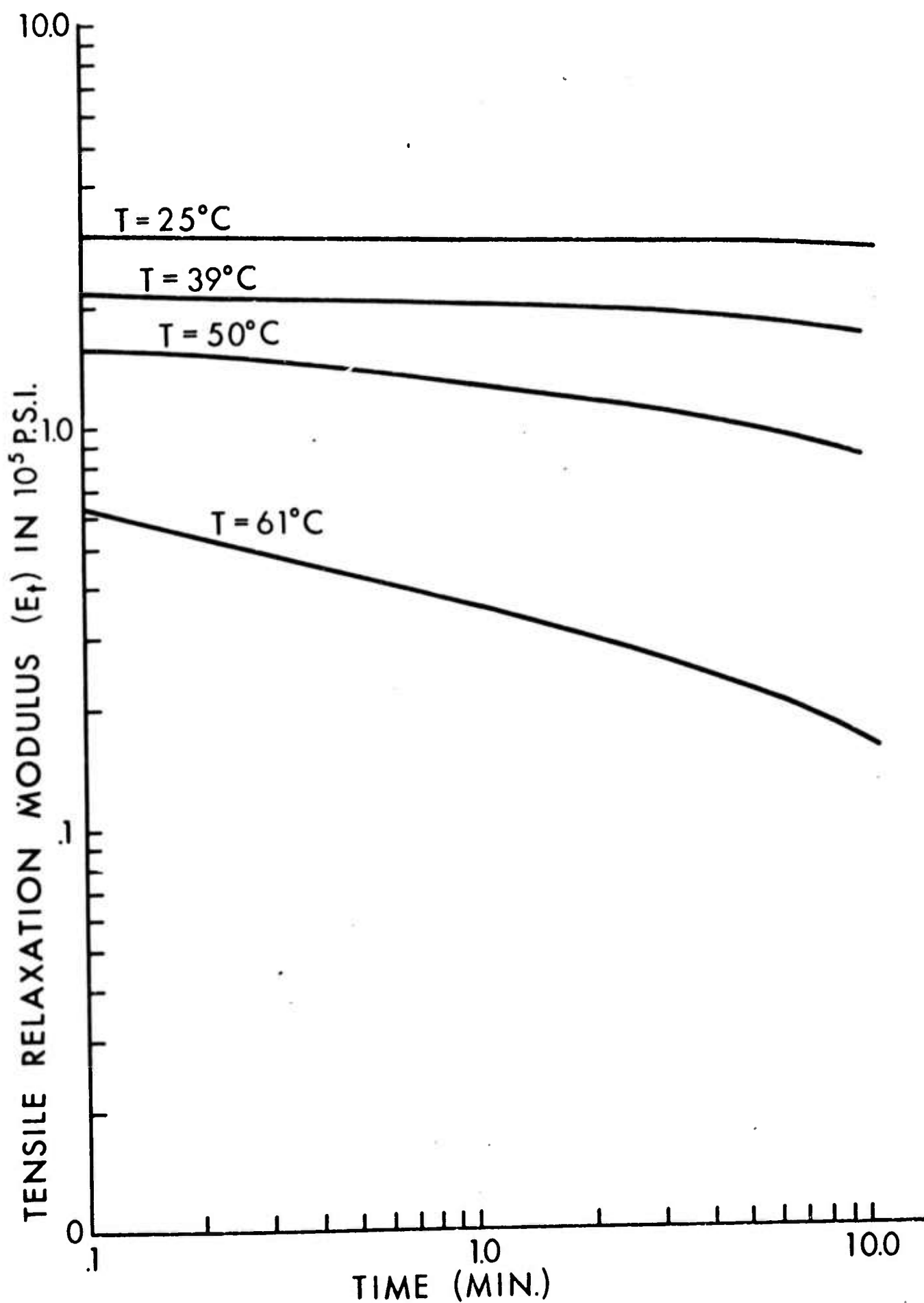


FIGURE 10 TYPICAL RELAXATION MODULUS VS TIME CURVES FOR DIFFERENT TEMPERATURE LEVELS FOR THE 60/40 EPOXY-VERSALID MIX.

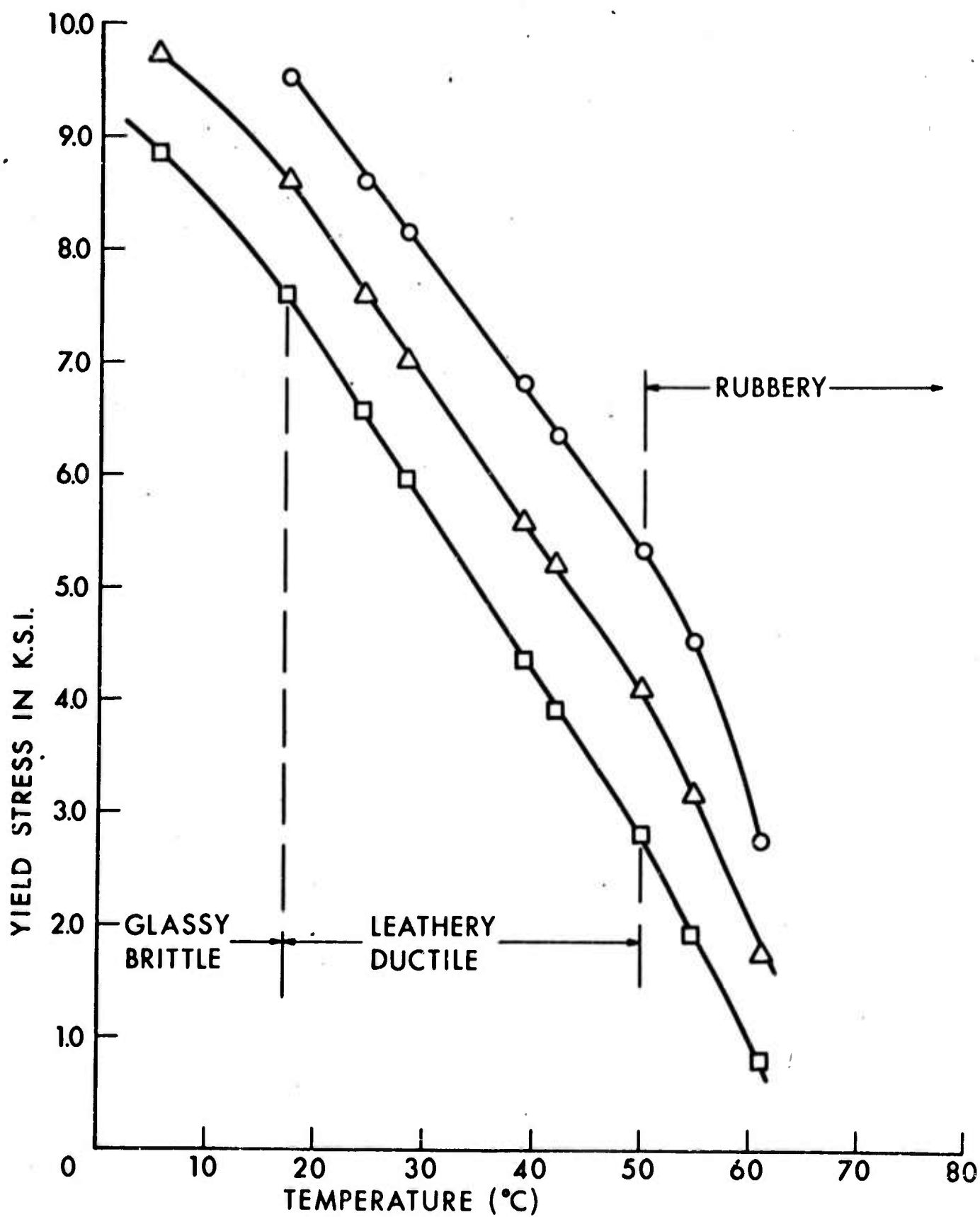


FIGURE 11A THE DEPENDENCE OF YIELD STRESS ON TEMPERATURE UNDER DIFFERENT C.S.R. LEVELS FOR THE EPOXY-VERSATIC SYSTEMS OF 60/40 MIX.

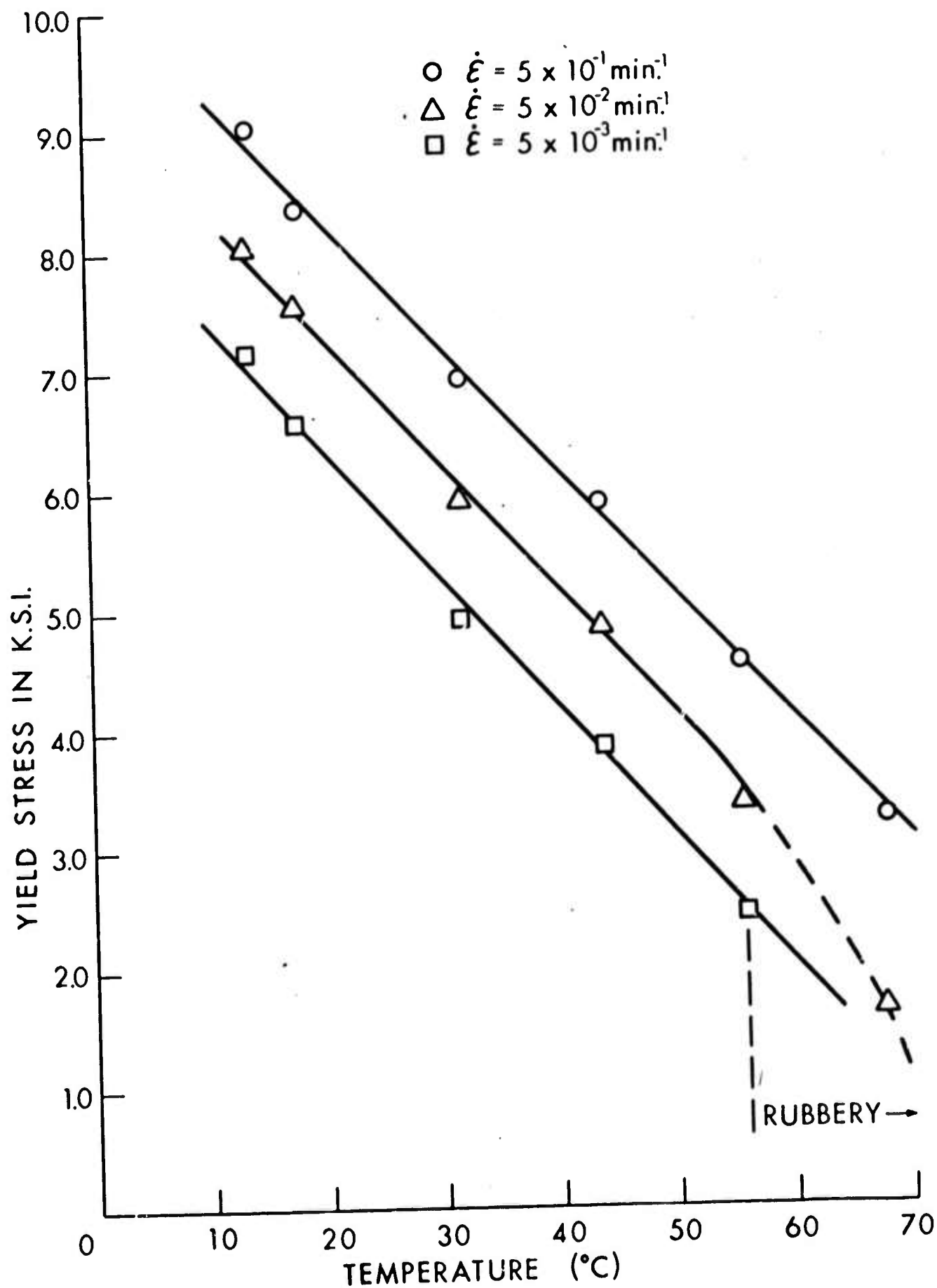


FIGURE 11B THE DEPENDENCE OF YIELD STRESS ON TEMPERATURE UNDER DIFFERENT C.S.R. LEVELS FOR THE EPOXY-VERSAMID SYSTEMS OF 70/30 MIX.

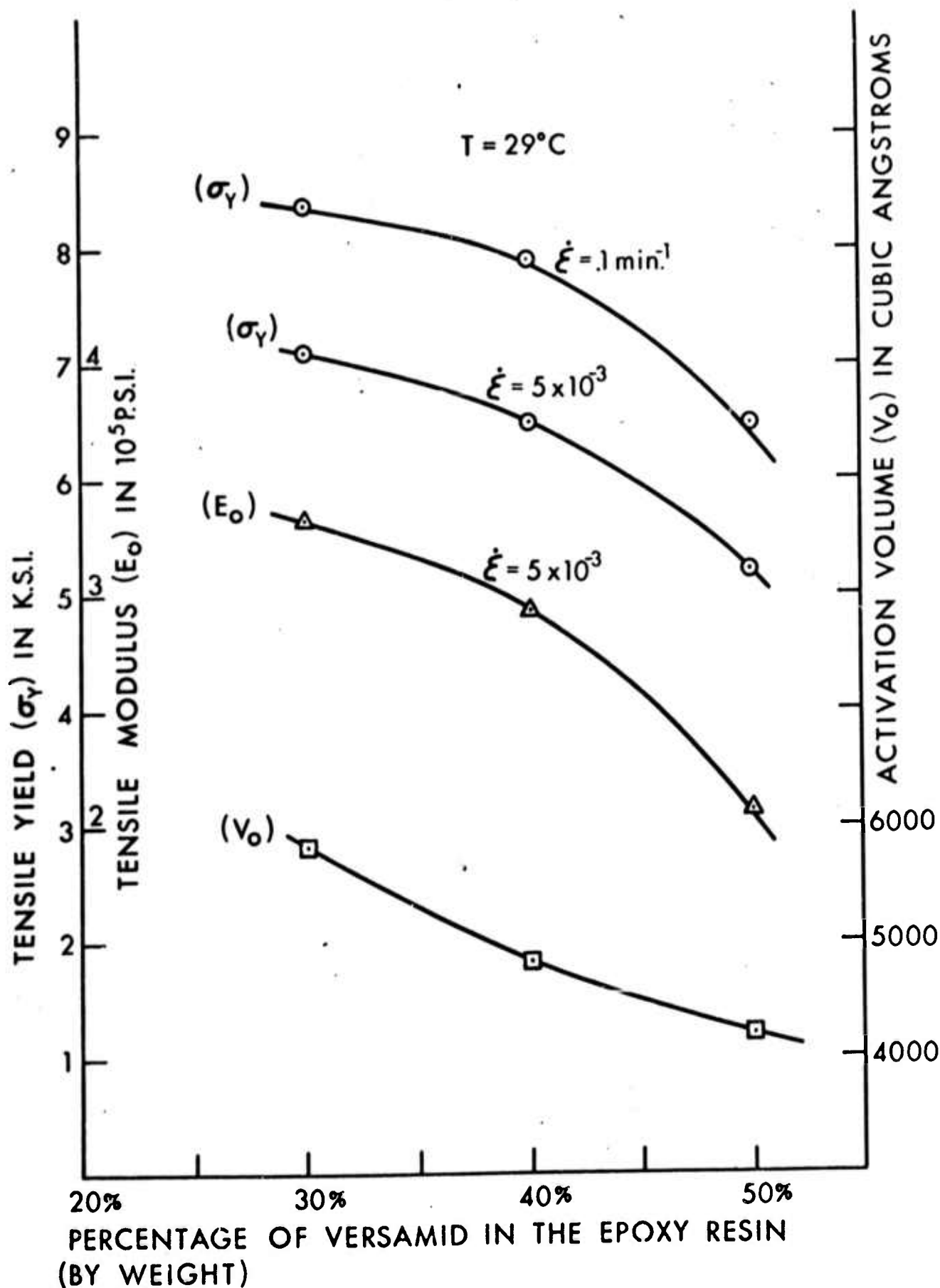


FIGURE 12 THE EFFECT OF VERSAMID CONTENT IN THE EPOXY RESIN ON THE ACTIVATION VOLUME AND ON MECHANICAL CHARACTERISTICS.



## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)

Monsanto Research Corporation

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3 REPORT TITLE

The Effect of Temperature on the Delayed Yield and Failure of "Plasticized" Epoxy Resin

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (First name, middle initial, last name)

O. Ishai

6 REPORT DATE

September 1968

7a. TOTAL NO. OF PAGES

41

7b. NO. OF REFS

29

8a. CONTRACT OR GRANT NO.

N00014-67-C-0218

h. PROJECT NO.

9a. ORIGINATOR'S REPORT NUMBER(S)

HPC 68-59

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nations may be made only with prior approval of the Director of Material Sciences, Office of Naval Research.

11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY

Office of Naval Research  
Washington, D. C. 20360

13 ABSTRACT

→ Epoxy-versamid specimens were loaded in tension up to failure at different constant strain-rates and temperatures. Results revealed three modes of behavior prevailing at different temperature-strain-rate regions and associated with brittle, ductile and rubbery failure modes. The ductile region was found to be confined within a narrow band on the temperature-strain-rate plane, and is characterized by a yield plateau in the stress-strain curve and by linear dependence of yield stress on log strain rate and temperature. Yield strain seems to be almost unaffected by strain-rate, but decreases slightly with temperature rise.

Analysis indicated that experimental data within the ductile region are consistent with Eyring's formulation for non-Newtonian viscoplastic flow. It leads to the evaluation of the "apparent activation energy" and activation volume for the two epoxy systems tested.

Comparison with previous work indicates that the above parameters as well as yield stress and elastic modulus tend to increase with the decrease of the versamid content in the resin.

## KEY WORDS

## LINK A

## LINK B

## LINK C

ROLE

WT

ROLE

WT

ROLE

WT

temperature effect

strain-rate effect

yield stress, yield strain

brittle failure

epoxy resin

tension

tangent modulus

relaxation